

# Fate of Chlorsulfuron in the Environment.

## 2. Field Evaluations

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**Abstract:** The fate and mobility of chlorsulfuron was determined in several field studies with  $^{14}\text{C}$ -labeled chlorsulfuron. A study comparing fall with spring applications ( $\sim 100 \text{ g AI ha}^{-1}$ ) to *in-situ* soil columns (35 cm depth) in neutral to alkaline soils (pH 6.9–8.2, OM 1.0–5.3) located in CO, ID and ND demonstrated that fall treatments did not persist longer into the following year than spring treatments. Mobility into the soil profile appeared to be initially faster following fall applications at the ID and ND sites, but differences between application seasons appeared to moderate with time. A field-soil metabolism study conducted at Madera, CA on a sandy loam soil (pH 6.3–6.9 and 0.3–0.4% OM with depth) with chlorsulfuron ( $\sim 158 \text{ g AI ha}^{-1}$ ) demonstrated rapid dissipation of chlorsulfuron (pseudo-first-order half-life 18 days). No intact chlorsulfuron was found after the 120-day sampling. Major metabolites observed in this study were chlorobenzenesulfonamide (2-chlorobenzenesulfonamide) and triazine amine (4-methoxy-6-methyl-1,3,5-triazin-2-amine), products of bridge cleavage, and *O*-desmethylchlorsulfuron (1-(2-chlorophenylsulfonyl)-3-(4-hydroxy-6-methyl-1,3,5-triazin-2-yl)urea). No intact chlorsulfuron was detected below the 0–15 cm layer at any sampling (maximum depth 60–90 cm), but chlorobenzenesulfonamide and ring-opened carbamoyl guanidine (1-(2-chlorophenylsulfonyl)-3-(ureido-imino)urea) were found at the 15–30 cm depth. In a similar study conducted on a silt loam soil in Moscow, ID (pH 6.1–6.9 and 2.2–1.0% OM with depth), overall dissipation was much slower than at Madera, CA due to the cooler climate (average soil temperature  $8.6^\circ$  versus  $20.0^\circ$ ). The initial rate of chlorsulfuron dissipation was similar (pseudo-first-order half-life 18 days), but dissipation exhibited a distinctly slower second stage (half-life 109 days) not exhibited at Madera, CA. By the 370-day sampling no intact chlorsulfuron was detected. The chlorobenzenesulfonamide and triazine amine were the major metabolites found in this study, accounting for approximately 38 and 30%, respectively, of the initial chlorsulfuron at the last sampling (571 days). Other metabolites were found in lesser amounts, including *O*-desmethylchlorsulfuron, ring-opened carbamoyl guanidine, hydroxy triazine amine (4-amino-6-methyl-1,3,5-triazine-2-ol), triazine urea ((4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea), an undifferentiated bound fraction and an unidentified group of polar components. The presence of triazine urea indicates that soil-surface photolysis (or indirect photolysis) may have been operative. In the study in Moscow, ID, no intact chlorsulfuron was found below the 0–15 cm layer at any sampling (maximum depth 75 cm). Movement of total radioactive components was restricted to a maximum depth of 60 cm at Madera, CA and 50 cm at Moscow, ID. The overall water balance over the duration of both studies was negative, helping to explain the observed lack of leaching. The PRZM3 model was used to predict the distribution profile of chlorsulfuron at the Moscow, ID site for which the base case overpredicted leaching (down to 20–30 cm) and predicted the depletion of the surface layer, which did not occur. The prediction was improved by arbitrarily doubling the  $K_{oc}$  value and using a slightly higher than measured soil bulk density. © 1998 SCI

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Key words: chlorsulfuron; degradation; dissipation; environmental fate; field dissipation; leaching; metabolites; modeling; PRZM3; sulfonylureas

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## 1 INTRODUCTION

Chlorsulfuron (Fig. 1; 1), used in the variety of climates where cereals are grown, is considered to be only moderately persistent in soil.<sup>1,2</sup> However, in certain regions of the world (i.e. central and northern Great Plains of North America) label restrictions on what crop can be planted in the year(s) after an application have had to be included because of potential carry-over under particular circumstances (i.e. soil pH > 7.5). Injury to rotational crops can be related to the high degree of sensitivity of certain plant species to extremely low chlorsulfuron levels.<sup>1,3,4</sup> The effects of soil pH and texture, and of precipitation upon rates of chlorsulfuron dissipation are well-known.<sup>1,5-15</sup> Because most field studies investigating longevity in soils have been conducted using bioassays,<sup>5-7,9,11,15-23</sup> and few have been conducted using chemical assays,<sup>8,12,14,24,25</sup> relatively little information on degradation mechanisms other than aqueous hydrolysis<sup>3,26</sup> has been published for chlorsulfuron. Some researchers have compared relative persistence following fall and spring applications to determine the effect of application season upon the longevity of weed control. Eleftherohorinos and Kotoula-Syka<sup>19</sup> stated that pre-emergence applications made to a pH 7.4 soil in Greece in December persisted longer into the season than post-emergent applications made to wheat the following spring in March or April. Nilsson<sup>20</sup> reported an increase from 5.5 to 7.5 months of persistence of bioactivity against *Sinapis alba* L. from

fall-applied versus spring-applied chlorsulfuron treatments.

The mobility of chlorsulfuron has been studied extensively in field soils,<sup>7,9,11,13,15,16,20,27-29</sup> also using mainly bioassays to determine depth of leaching and amounts leached. Prediction of chlorsulfuron mobility intuitively from behavior in laboratory experiments or empirically from models using chemical and physical parameters generated from such studies is not always consistent with actual field behavior. In field experiments on slightly acidic to alkaline soils (pH 6.5-7.9) in England using a lettuce (*Lactuca sativa* L.) bioassay to detect chlorsulfuron, Blair *et al.*<sup>16</sup> and Walker and Welch<sup>15</sup> found that almost all of the chlorsulfuron bioactivity remained in the upper 50 cm of soil and that a significant proportion remained in the upper 10 cm. Their model predicted movement of chlorsulfuron to lower depths than actually found and depletion of the upper 10 cm, which did not occur.

Although laboratory mobility studies, as in those conducted in the companion paper,<sup>30</sup> indicate the capability for a high level of soil migration by chlorsulfuron, they have limitations when used to predict behavior in the field. In addition to chemical and physical properties of the chemical and soil, the effect of the local climate upon dissipation rate and mobility must be factored in. Models are an accepted tool which try to bridge the gap between laboratory predictions and field behavior. In order to characterize the metabolism and mobility of chlorsulfuron in field soils, studies were

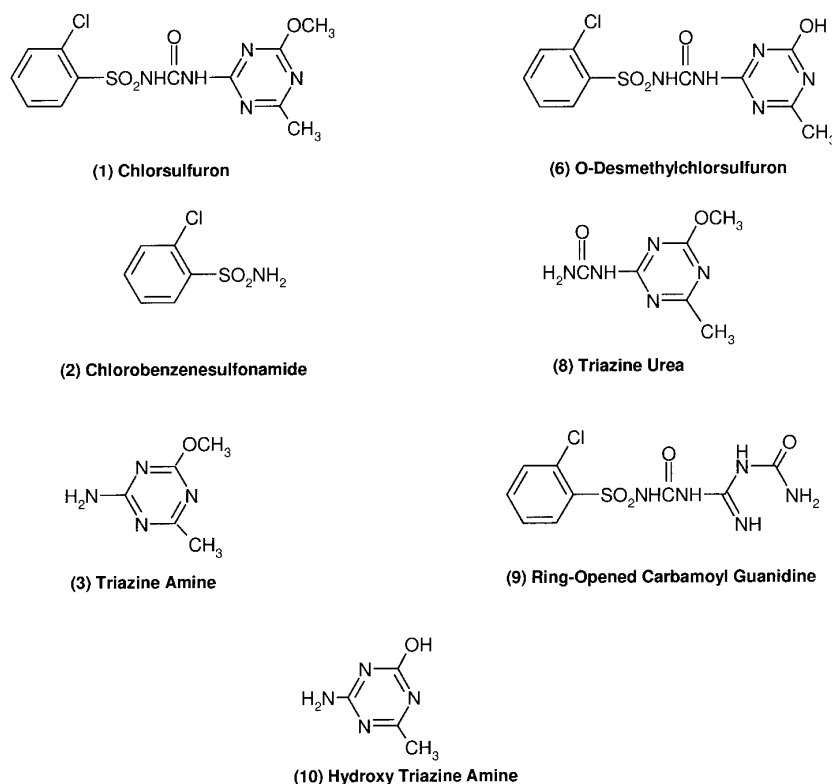


Fig. 1. Structures of chlorsulfuron and major metabolites found in field studies.

undertaken with  $^{14}\text{C}$ -labeled chlorsulfuron. Prediction of field behavior using laboratory data fed into the PRZM3 model<sup>31</sup> was employed to determine the suitability of key laboratory data as modeling parameters.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Field soil dissipation and metabolism

#### 2.1.1 Field dissipation and mobility studies—effect of season of application

The dissipation of fall versus spring applications of chlorsulfuron was followed in the field at three locations—Akron, Colorado (CO), Kimberley, Idaho (ID) and Fargo, North Dakota (ND) (Rapisarda, C. &

Scott, M. T., Field dissipation studies with [*phenyl-U- $^{14}\text{C}$* ]chlorsulfuron in US and Canadian soils. *DuPont Internal Report*, AMR 307-84, Rev. 2, 1984). The Akron, CO location included a neutral pH site and an alkaline pH site, located in different sections of the same field. Selected soil properties are listed in Table 1 and application dates are listed in Table 2. Soil columns consisted of stainless steel cylinders (10 cm ID, 38 cm length) driven into the ground until approximately 3 cm protruded above the surface to contain rain water and minimize potential run-off losses. Approximately 1.0 mg of [*phenyl-U- $^{14}\text{C}$* ]chlorsulfuron (0.162 kBq mg<sup>-1</sup>, >99% purity) was applied to the soil surface contained in the cylinder by pipette (5 ml application volume), giving an approximate application rate of 100 g AI ha<sup>-1</sup> (0.1–0.3 mg kg<sup>-1</sup> in the top 15 cm of the various

**TABLE 1**  
Properties of the Soils Used in the  $^{14}\text{C}$  Dissipation and Field Mobility Studies

Location	Depth (cm)	Organic matter (%)	pH <sub>water</sub>	Sand (%)	Silt (%)	Clay (%)	Cation exchange capacity (meq 100 g <sup>-1</sup> )	Texture	Bulk Density (g cm <sup>-3</sup> )	Moisture holding capacity at 1/3 bar (%)
Akron, CO	0–35	1.0	6.9	36	50	14	14.2	Silt loam	—	—
Akron, CO	0–35	1.2	8.2	21	62	17	10.3	Silt loam	—	—
Kimberley, ID	0–35	1.3	8.0	6	77	17	17.4	Silt loam	—	—
Fargo, ND	0–35	5.3	7.6	0	67	33	46.2	Silty clay	—	—
Madera, CA	0–15	0.4	6.3	75	17	8	3.3	Sandy	1.51	6.30
	15–30	0.3	6.7	75	17	8	2.8	Sandy	1.53	6.25
	30–45	0.3	6.9	77	16	7	2.8	Loamy	1.54	6.04
	45–60	0.3	6.7	77	16	7	2.9	Loamy	1.49	6.09
	60–75	0.4	6.6	77	16	7	3.5	Loamy	1.58	6.20
	75–90	0.3	6.9	77	16	7	3.4	Loamy	1.57	6.54
Moscow, ID	0–10	2.2	6.1	11	64	25	21.1	Silt loam	1.09	27.3
	10–20	1.9	6.3	12	61	27	22.0	Silty clay	1.06	24.8
	20–30	1.6	6.5	12	59	29	21.9	Silty clay	1.00	26.8
	30–45	1.3	6.7	9	66	25	21.9	Silt loam	1.03	31.2
	45–60	1.2	6.8	11	66	23	21.1	Silt loam	1.00	30.4
	60–75	1.0	6.9	11	64	25	21.9	Silt loam	0.72	31.3

**TABLE 2**  
Selected Soil Properties and Application Dates for  $^{14}\text{C}$ -Labeled Chlorsulfuron Field Dissipation Studies

Study location	Application dates	Application season	Sampling intervals (days)
Akron, CO (neutral pH)	6 Nov. 1982	Fall	0, 30, 152, 228, 289, 365, 593, 791, 1186, 1430
	12 May 1983	Spring	0, 39, 84, 120, 174, 354, 540, 969
Akron, CO (alkaline pH)	12 Nov. 1982	Fall	0, 24, 137, 222, 289, 365, 593, 785, 1186, 1430
	12 May 1983	Spring	0, 39, 84, 120, 174, 354, 540, 969
Kimberley, ID	4 Nov. 1982	Fall	0, 30, 120, 240, 300, 360, 570, 1290
	6 May 1983	Spring	0, 21, 30, 60, 120, 180, 390, 540, 1110
Fargo, ND	12 Nov. 1982	Fall	0, 162, 240, 360, 570, 729, 900, 1080, 1410
	7 June 1983	Spring	0, 15, 39, 60, 129, 300, 390, 480, 840, 1200
Madera, CA	21 Mar. 1989	Spring	0, 3, 7, 14, 30, 59, 120, 210, 240, 300, 331, 391, 450, 540
Moscow, ID	4 June 1992	Spring	0, 4, 7, 14, 41, 70, 123, 272, 370, 571

soils). Immediately after application, 50 ml of water (equivalent to 6 mm of precipitation) was added to the soil surface, which was then covered with approximately 1 cm of untreated soil to minimize losses through wind erosion. The soil columns were harvested according to the intervals shown in Table 2, frozen, and shipped to the DuPont Experimental Station for later analysis. The columns were sectioned into 0–5, 5–12, 12–22 and 22–35-cm segments, allowed to air-dry, homogenized, ground and combusted (Oximat® Sample Oxidizer, Model OX300, R. J. Harvey Instrument Co., Hillsdale, NJ) and counted by LSC (Tracor Mark III Scintillation Counter, Model 6881, TM Analytic, Inc., Elk Grove, IL). When detectable radioactivity was found (detection limit <1% of applied radioactivity) aliquots of the soil (200–1200 g) were extracted by percolating acetone + 0.1 M aqueous ammonium carbonate (9 + 1 by volume) overnight through the soil (1 + 2, soil + solvent, weight to volume). The soil was then further extracted with 0.1 M aqueous ammonium carbonate for 1 h at 50°C in an ultrasonic bath, the soil slurries were centrifuged for 15 min at 2500 rev min<sup>-1</sup>, the supernatant solutions decanted, and the pellets extracted for 15 min at 50°C in an ultrasonic bath with acetone. All solutions were combined, counted for radioactivity by LSC, developed on TLC plates (silica gel, 300–1700 µm, Analtech, Inc., Newark, Delaware) developed to 15 cm in dichloromethane + methanol + 1 M ammonium hydroxide (170 + 27 + 3 by volume), for which autoradiograms were obtained (SB-5 X-ray film, Eastman Kodak, Rochester, New York). Radioactive areas located on the TLC plates were removed and counted for total radioactivity by LSC. Identification and quantification of substance was limited to chlorsulfuron. Extracted soils were combusted and total radioactivity was determined by LSC.

### 2.1.2 Field metabolism and mobility studies

**2.1.2.1 Madera, CA.** To determine the dissipation and potential for mobility in a light-textured soil receiving regular additions of water through irrigation, a study was conducted in the San Joaquin Valley of California (Dietrich, R. F. & Taylor, G. T., Terrestrial field dissipation of *phenyl-U-<sup>14</sup>C*-DPX-W4189 and *triazine-<sup>14</sup>C*-DPX-W4189 in Madera, CA. *DuPont Internal Report*, AMR 1417-89, 1989). The site was located on a Madera sandy loam soil (Table 1) located near Madera, CA which had been fallow since 1980 and had not been treated with pesticides since that time, with a depth to the water table of approximately 30 m. For this study, the soil columns consisted of stainless steel cylinders lined with plastic sleeves (9.5 cm ID, 96.5 cm length) driven into the ground until approximately 2.5–5 cm protruded above the surface to contain rain and irrigation water and minimize potential run-off losses. Topsoil was added from the surrounding area to bring

the surface, compacted by driving the cylinders into the soil, up to the level of the surrounding soil. Approximately 0.1 mg of either [*phenyl-U-<sup>14</sup>C*]chlorsulfuron (0.643 kBq mg<sup>-1</sup>, >95% purity) or [*triazine-2-<sup>14</sup>C*]chlorsulfuron (0.411 kBq mg<sup>-1</sup>, >95% purity) dissolved in pH 7.0, 0.1 M Na<sub>2</sub>HPO<sub>4</sub> buffer, formulation ingredients and distilled water was applied to the soil surface in the cylinder by pipette (5 ml application volume), giving an approximate application rate of 158 g AI ha<sup>-1</sup> (0.06 mg kg<sup>-1</sup> in the top 15 cm of soil). Each radiolabel was applied separately to a soil column to allow monitoring of the major breakdown products. Irrigation was provided by overhead sprinkler from a nearby well at approximately two-week intervals (see Fig. 10). Weather data (daily soil temperature maxima and minima at 5 cm depth and precipitation) were collected at the site, with the exception of pan-evaporation data, which was collected at a site approximately 32 km to the south. For the calculation of water balance, pan-evaporation data were multiplied by a factor of 0.75 to calculate estimated soil evaporation.<sup>32</sup>

At selected intervals after treatment (see Table 2), one randomly selected cylinder of each radiolabeled compound was removed from the plot, then sectioned into 15-cm segments and frozen. For the last two samplings, three 60-cm-long soil cores were taken from below the bottom of the cylinders (total sampling depth 1.5 m) and sectioned into 15-cm segments. Samples from the first two weeks after treatment were homogenized with dry ice, air-dried and stored frozen prior to analysis. For other samples, aliquots (50 g) were removed and stored frozen for later analysis; the remaining sample was air-dried prior to analysis. To determine total radioactivity, triplicate samples (0.25 g) of the air-dried soil were analyzed by combustion as described previously. When detectable radioactivity (detection limit = ~5% of applied radioactivity) was found in soil samples, 50-g aliquots were extracted three times with 100 ml portions of acetone + 0.1 M aqueous ammonium carbonate (90 + 10 by volume) with agitation provided by a ultrasonic bath maintained at 50°C. The slurry was centrifuged (2000 rev min<sup>-1</sup>, 10 min) and the supernatant was decanted. The remaining soil was further extracted with 100 ml of 0.1 M ammonium carbonate for 1 h in an ultrasonic bath maintained at 50°C.

The combined extracts were concentrated by rotary evaporation and analyzed for total radioactivity by LSC. Soil extracts were analyzed by HPLC (HPLC: Varian Vista 5560, Varian Associates, Palo Alto, CA; injection volume: 1000 µl; column: 4.6 mm × 25 cm Zorbax® RX (Mac-Mod Analytical, Inc., Chadds Ford, PA); guard column: 4.6 × 30 mm RP-18 (Brownlee Labs, Emeryville, CA; temp. 40°C; mobile phase: (A) acetonitrile + 0.1% H<sub>3</sub>PO<sub>4</sub> (by volume), (B) water + 0.1% H<sub>3</sub>PO<sub>4</sub> (by volume); gradient (min/%A): 0–1/0, 31/45, 33–35/100, 36–46/0). Radiochromatog-

rams of these aqueous solutions were obtained by LSC of 0.5-min eluate fractions collected on an ISCO Foxy® fraction collector (ISCO, Inc., Lincoln, Nebraska). Identification of radioactive peaks was made by comparison of retention times with those of chromatographed non-radiolabeled standards of suspected degradation products (monitored by a UV detector). Identification of the structure of metabolite (9), the ring-opened carbamoyl guanidine, was based on mass spectral and NMR characterizations. Extracted soil was analyzed by combustion/LSC to quantify unextractable (bound) residues.

**2.1.2.2 Moscow, ID.** To determine the dissipation and mobility for chlorsulfuron in a moister and cooler climate than found at the Madera, CA site, a study was conducted in the Pacific Northwest (Rhodes, B. C., *Terrestrial field dissipation of <sup>14</sup>C-chlorsulfuron*. DuPont Internal Report, 2266-91, 1991). The site was located on a Palouse-Latahco silt loam soil (see Table 1) on a permanent grass plot at the University of Idaho Research Farm near Moscow, ID with the permanent water table approximately 6 m below the surface. The experimental set-up and treatment solutions and rates were similar to the experiment at the Madera, CA site (Section 2.1.2.1), giving an approximate application rate of 158 g AI ha<sup>-1</sup> (0.126 mg kg<sup>-1</sup> in the top 10 cm of soil). Weather data (daily soil temperature maxima and minima at 10 cm depth, precipitation, and pan-evaporation) were collected at the site. One randomly selected cylinder of each radiolabeled compound was taken out of the ground at the intervals listed in Table 2 and sectioned into 10-cm segments. A soil core was taken from the bottom of the extracted cylinder core to a depth of 45 cm (total sampling depth 75 cm) and sectioned into 15-cm segments. When radioactivity detected by combustion (detection limit <1% of applied radioactivity) was found in soil segments, 75-g aliquots were extracted twice by shaking with 100 ml of methylene chloride + methanol (1 + 1 by volume) for 30 min. The supernatants were decanted with filtration after centrifugation and pooled, analyzed by LSC and concentrated (extract A). The extracted soil was further extracted twice using 100 ml of methanol + 0.1 M ammonium carbonate (1 + 1 by volume) as above (extract B). The soil pellet was then exhaustively extracted by shaking for three or more hours in 175 ml of acetone + 1 M HCl + 10 g litre<sup>-1</sup> Triton® X-100 surfactant (70 + 15 + 15 by volume) and the supernatant was decanted with filtration, counted by LSC, concentrated to near dryness and redissolved in acetonitrile + water. The exhaustively-extracted soil was air-dried and analyzed by combustion/LSC to quantify unextractable (bound) residues.

Soil extracts were analyzed by HPLC as described previously in Section 2.1.2.1. Radiochromatograms of these aqueous solutions were obtained using a radioac-

tive flow monitor (Ramona-LS, Raytest, IN/US Service Corporation, Fairfield, NJ). Identification of radioactive peaks was made by comparison of retention times with those of chromatographed non-radiolabeled standards of suspected degradation products (monitored by a UV detector). Selected extracts were also analyzed by TLC/radiochromatography (250 and 500 m, Merck Kieselgel F-254 plates (E. Merck, Darmstadt, Germany); developed to 15 cm with methylene chloride + methanol + 9 M ammonium hydroxide (170 + 27 + 3 by volume) to confirm identities of metabolites based upon HPLC identification.

## 2.2 Modeling

The dissipation and mobility of chlorsulfuron (parent only) at the Moscow, ID site were predicted using the PRZM3 model.<sup>31</sup> Actual weather data from the field dissipation experiment (see Fig. 13) were used for all runs. For the base case, the measured bulk density of 1.1 g in the top 10 cm of soil and a  $K_{oc}$  of 54 from the batch equilibrium experiments<sup>30</sup> were used. A first-order half-life for chlorsulfuron of 18 days was calculated for days 0–41 and of 109 days for days 41–571 from the actual field data (see Fig. 4) to account for the two-stage dissipation pattern commonly seen for sulfonylureas in soils.<sup>33</sup> An initial chlorsulfuron application rate of 158 g AI ha<sup>-1</sup> was assumed, and levels below the lowest level of radiochemical detection (0.001 mg kg<sup>-1</sup>) were reported as zero.

## 2.3 Statistical analysis

All analyses were conducted using the procedures GLM and REG using SAS software.<sup>34</sup> Because chlorsulfuron dissipation in fall applications exhibited an initial lag before rapid dissipation,  $DT_{50}$  (time required for 50% dissipation) values were calculated using a logistic function:

$$y = C + ((D - C) \times (1 + e^{[b \times \log(Z) - \log(DT_{50})]})^{-1})$$

where  $C$  = lower limit,  $D$  = upper limit and  $Z$  = time after treatment.<sup>35</sup> Because the lower limit is zero, the term  $C$  drops away, and the equation can be rewritten as:

$$y = D \times (1 + e^{[b \times \log(Z) - \log(DT_{50})]})^{-1}$$

The low number of sampling points and lack of appropriate samplings which established the onset of rapid springtime degradation precluded using other equations which would have overestimated the degradation rate during the initial rapid phase and involved arbitrarily choosing a time point in spring for the fall applications at which to being the rapid dissipation phase. The logistic function allowed the use of one equation to determine the  $DT_{50}$  for both fall and spring applications.

### 3 RESULTS AND DISCUSSION

#### 3.1 Field soil dissipation

##### 3.1.1 Field dissipation studies—effect of season of application

A comparison of the fall and spring treatments (Fig. 2) shows that fall treatments generally dissipated more quickly, reaching levels <10% of applied sooner in the year than the spring treatments at all sites except at Fargo, ND, where the treatments appeared to dissipate in a similar manner. The decline curves for fall treatments (which were cut off at a maximum of 620 days) indicate an initial, slower dissipation phase during the winter followed by a rapid dissipation phase during spring and summer. Spring treatments showed a rapid initiation of degradation which slowed at the onset of the subsequent fall or depletion of chlorsulfuron. The average  $DT_{50}$  value (Table 3) was 49 days for spring treatments and 192 days for fall treatments, which account for the effect of winter. The logistic function appeared to describe the dissipation curves adequately, with  $R^2$  values of 0.726 to 0.947 (Table 3); however, in some cases the functions diverged significantly from the

measured chlorsulfuron residues in the period >1 year after treatment (e.g. Kimberley, ID fall treatment). The rates of decline during the spring and summer appeared similar between fall and spring treatments except at the Akron, CO neutral pH site, where the fall treatment appeared to dissipate more slowly. The comparison of the rates of decline in the fall treatments between the high- and neutral-pH sites at Akron, CO suggested that degradation was faster at the high-pH site, although the greater loss of radioactivity from the columns through leaching attributable to alkaline soils cannot be ruled out (see Section 3.2.1). This did not appear to be the case in the comparison between the spring treatments, where significantly higher chlorsulfuron residues were found during the October sampling at the high-pH versus neutral-pH site (>30% versus <5%, respectively).

These findings differ from those of Eleftherohorinos and Kotoula-Syka,<sup>19</sup> who applied chlorsulfuron to a wheat crop but did not discuss whether the potential reduction of the initial amount reaching the soil due to crop interception (in the spring treatments) was accounted for, which may explain the perceived increase in persistence from the pre-emergent fall applications made to bare ground. Nilsson<sup>20</sup> reported an increase

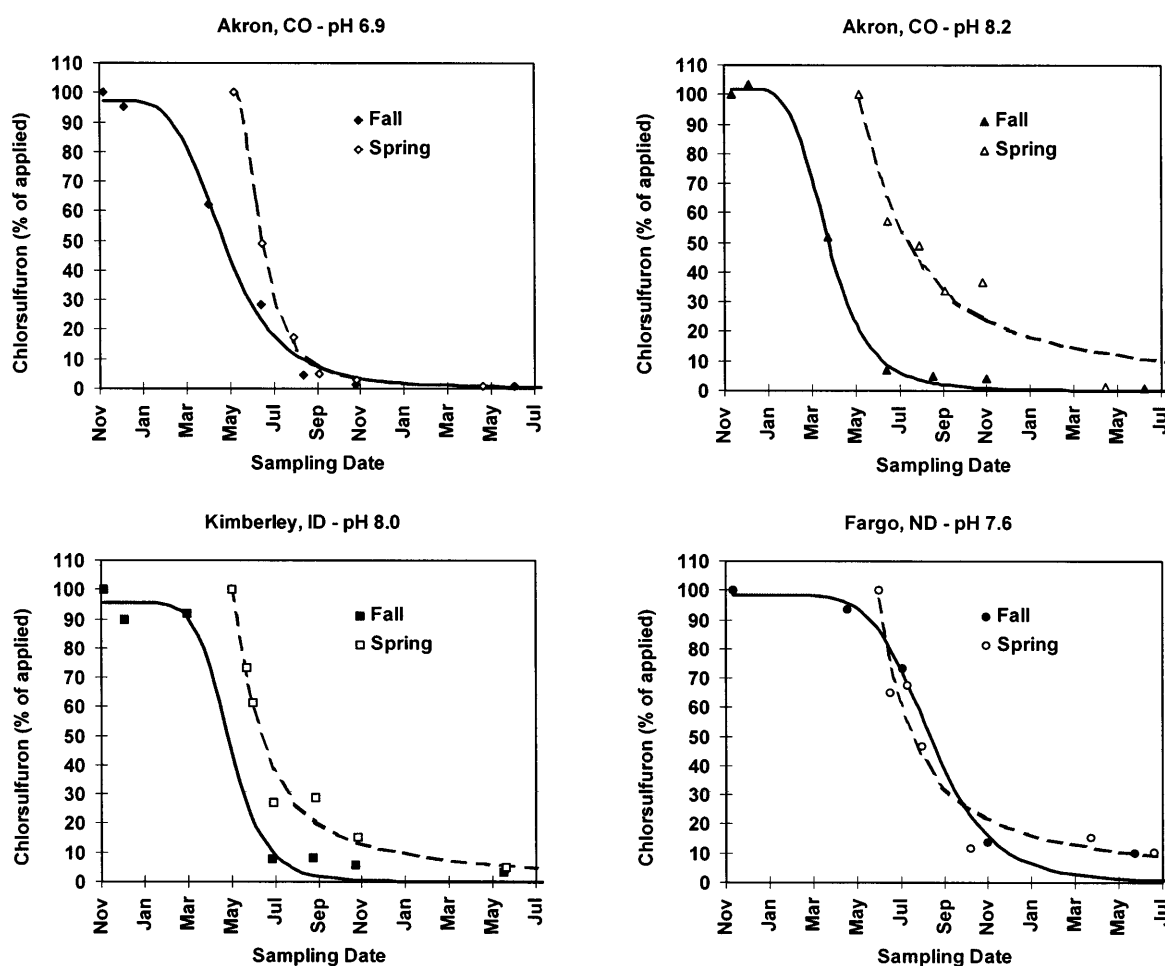


Fig. 2. Recovery of total applied radioactivity as [*phenyl-U-<sup>14</sup>C]chlorsulfuron from fall and spring applications to columns (35 cm) of neutral to alkaline soils at four field sites in the US. Lines represent predictions based upon logistic functions.*

**TABLE 3**  
Calculated DT<sub>50</sub> Values for Chlorsulfuron in Field Studies on Neutral to Alkaline Soils Applied in Fall or Spring Seasons and R<sup>2</sup> Values for Logistic Regression

Location	DT <sub>50</sub>		R <sup>2</sup>		Logistic function parameters <i>D</i> and <i>b</i> $y = D \times (1 + e^{[b \times \log(Z) - \log(DT_{50})]})^{-1}$			
					Application season			
	Fall	Spring	Fall	Spring	Fall		Spring	
	(days)				<i>D</i>	<i>b</i>	<i>D</i>	<i>b</i>
Akron, CO—pH 6.9	173	39	0.856	0.827	101.8	4.92	98.1	1.19
Akron, CO—pH 8.2	136	69	0.863	0.881	97.3	4.43	99.9	2.21
Kimberley, ID—pH 8.0	179	40	0.726	0.947	95.5	7.27	101.0	1.26
Fargo, ND—pH 7.6	280	49	0.780	0.900	98.4	6.55	97.0	1.10
Average	192	49						

of 5.5 to 7.5 months persistence from the fall application versus the spring application. Since the spring application occurred approximately five months after the fall application, it is difficult to ascertain whether the reported increase in persistence from the fall applications was significant or not. Overall persistence of the biological activity from fall and spring treatments was found to be similar in his study. In our studies, the fall treatments at all of the sites exhibited an initial lag in degradation, or decrease in rate, during the winter season due to the effect of lower soil temperatures on degradation processes (both aqueous hydrolysis and microbial degradation), after which the rate appeared to increase, apparently as soil temperatures rose with the onset of spring.

### 3.1.2 Field dissipation studies—soil metabolism

**3.1.2.1 Madera, CA.** Figure 3 shows the degradation of radiolabeled chlorsulfuron and the formation of key metabolites in an irrigated sandy loam soil located in Madera. Chlorsulfuron degraded rapidly to below the detection limit ( $<0.003 \text{ mg kg}^{-1}$ ) by the 120-day sampling. No intact chlorsulfuron was found below 0–15 cm at any sampling (maximum depth 90 cm). The dissipation appeared to follow simple pseudo-first-order kinetics (without two-stage behavior), with a half-life of 18 days, similar to the 20 days found for the first stage of degradation in the laboratory study (Section 3.2.1).<sup>30</sup> The lack of significant slowing of the dissipation rate after an initial stage of rapid degradation as in the laboratory study may be a consequence of the relatively high soil temperatures at this site, where the daily soil temperature maxima averaged 33.0°C for days 0–120 and 30.5°C for days 120–240 (see Fig. 10). This type of degradation (lacking a second, slower stage) was also observed in a study with Brazilian oxisols maintained at a relatively high temperature, 40°C.<sup>36</sup> The high temperatures, coupled with an abundance of soilwater (the site received a total of 283 mm precipitation, supple-

mented with 728 mm from bi-weekly irrigations) probably resulted in enhanced aqueous hydrolysis of chlorsulfuron before significant diffusion to sites of lesser reactivity or lesser availability to microbes could occur. A factor which potentially limited our ability to establish the portion of decline curve after the 120-day sampling was that the detection limit was at 5% of applied radioactivity.

The major metabolites of [*phenyl-U-<sup>14</sup>C]chlorsulfuron observed to form in detectable amounts were chlorobenzenesulfonamide (2) and ring-opened carbamoyl guanidine (9) (see Fig. 1 of Ref. 30 for structures and chemical names of all metabolites), and unidentified bound residues. No detectable amounts of *O*-desmethylchlorsulfuron (6) were found as in the laboratory aerobic soil metabolism study.<sup>30</sup> The level of (9) declined steadily during the 540-day sampling period, falling to 6.8% of the initially applied radioactivity. Detectable levels of (2) appeared at the 210-day sampling at the 15–30 cm depth, declined to levels below detection by the 300-day sampling, and reappeared at the 331-day sampling before declining again to below detection by the 540-day sampling.*

The results for [*triazine-2-<sup>14</sup>C]chlorsulfuron were similar to those for [*phenyl-U-<sup>14</sup>C]chlorsulfuron in this study, in which intact chlorsulfuron declined rapidly, falling below the detection limit by the 120-day sampling. The major metabolites formed in detectable amounts were triazine amine (3), (9), and unidentified bound residues. Low levels (~4% of applied) of an HPLC peak tentatively identified as triazine urea (8) were detected at the 59-day sampling (data not shown), but were not characterized further. Levels of (3) increased initially, but declined by the end of the study to 8.5% of the applied radioactivity. The level of (9) showed a steady decline at the 0–15 cm depth over the 540-day period to fall to 5.1% of the initially applied radioactivity. It first appeared in the sample taken at 15–30 cm at the 391-day sampling, but was declining at**

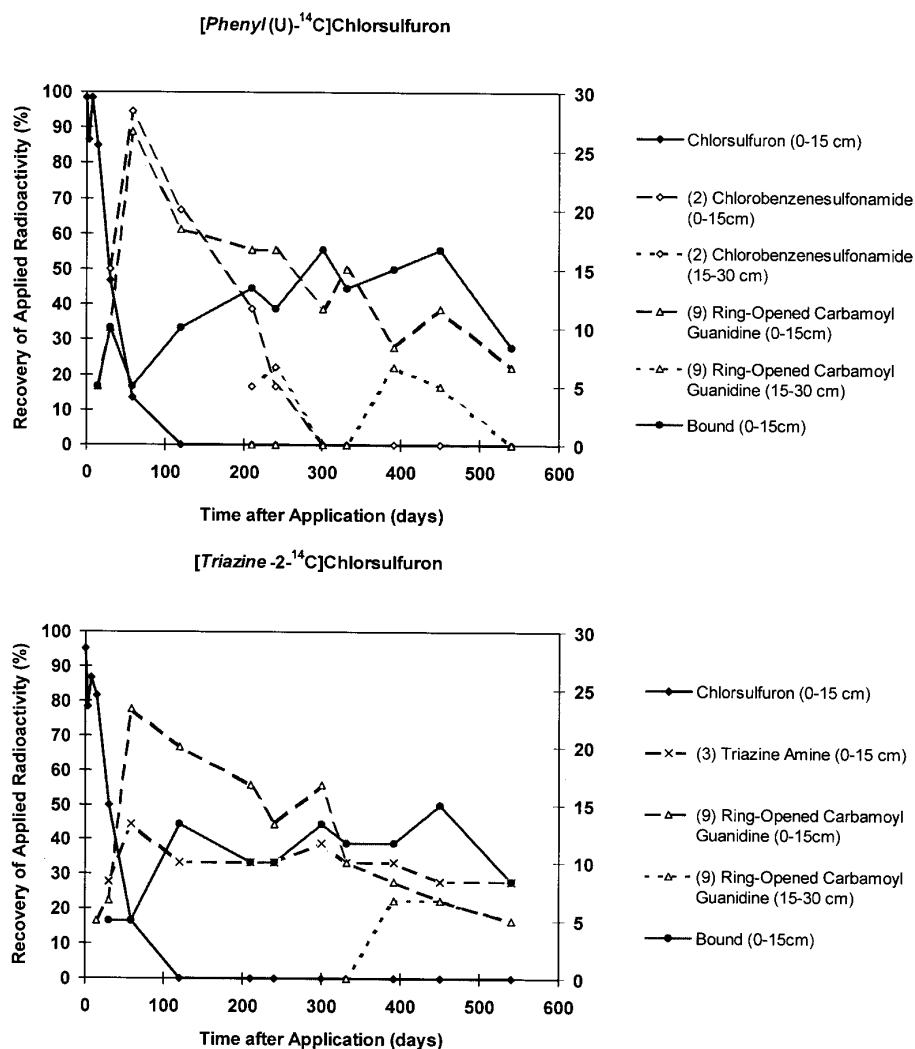


Fig. 3. Degradation of 158 g AI ha<sup>-1</sup> [*phenyl-U-<sup>14</sup>C]chlorsulfuron and [*triazine-2-<sup>14</sup>C]chlorsulfuron (0–100% scale to left) and formation of key metabolites (0–30% scale to right) in an irrigated field soil located in Madera, CA.**

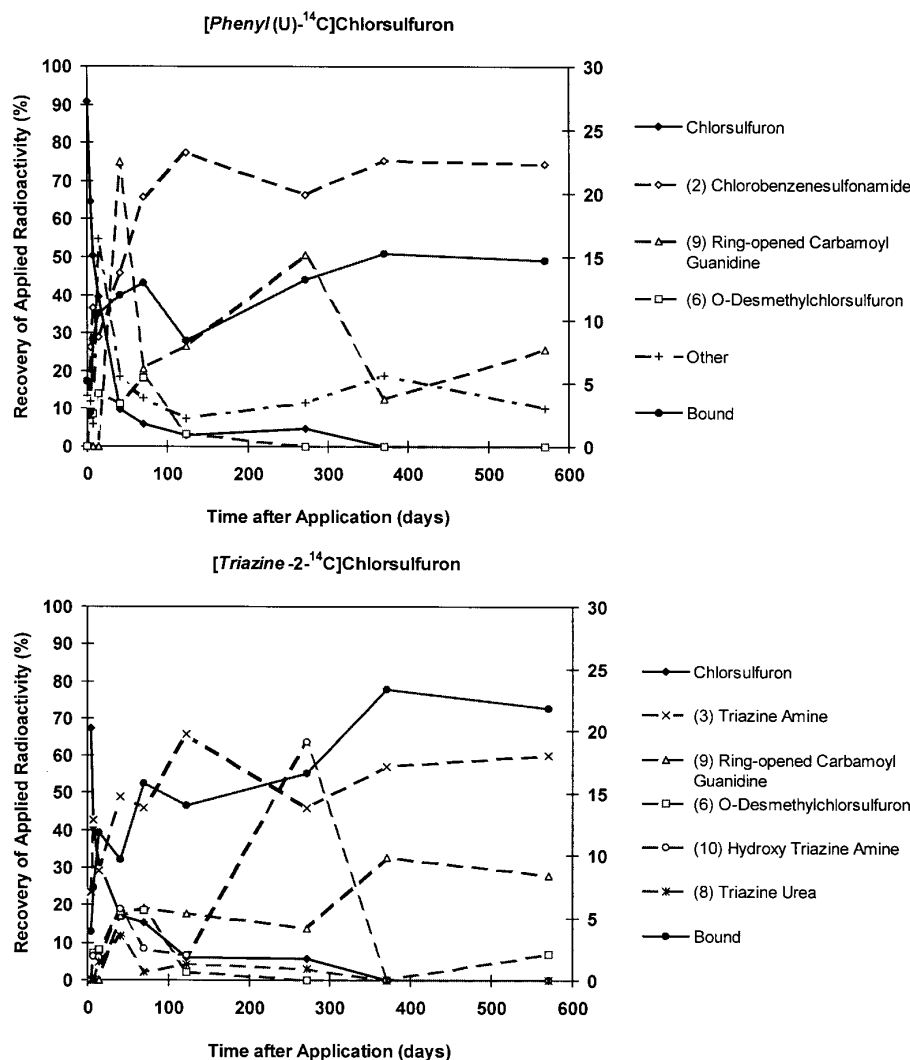
the end of the 540-day experiment. Unidentified forms of radioactivity bound to soil appeared to plateau and decline by the end of the 540-day period and comprised approximately 8% of initially-applied radioactivity for both the [*triazine-2-<sup>14</sup>C] and [*phenyl-U-<sup>14</sup>C]chlorsulfuron.**

**3.1.2.2 Moscow, ID.** The degradation and metabolism of chlorsulfuron were also followed at a site located in Moscow, ID in the northwestern US. Chlorsulfuron degraded to below the detection limit by the 370-day sampling (Fig. 4), persisting longer than observed at Madera, CA. Overall dissipation was slower in Moscow, ID than at the Madera, CA site despite the similar soil pH and is probably attributable to the cooler climate (see Figs 9 and 12), with 330 days out of 571 of soil temperature maxima below 20°C and 12 days above 35°C (versus 111 and 209 days, respectively, out of 539 at Madera, CA) and an average soil temperature maximum of 8.6° (versus 26.1 at Madera, CA). Dissipation appeared to follow a two-stage decline curve (in contrast to the Madera, CA study) with half-

lives of 18 and 109 days for the initial and second stages. The second, slower stage appeared to commence after the 41-day sampling, and demonstrated a slightly shorter half-life than that of the second stage in the aerobic soil-metabolism study (Section 3.2.1) conducted in the laboratory (128 days).<sup>30</sup> The daily temperature maxima averaged 26.6°C over days 0–123 and fell to 8.4°C over days 123–272, which would decrease microbial and hydrolytic rates during the latter stage. As observed at Madera, CA, no intact chlorsulfuron was found below the uppermost sampling increment (0–10 cm) at any sampling date. The site received a total of 1001 mm precipitation, supplemented with only 27 mm of irrigation (in two increments) to make up shortfalls from long-term monthly means (see Fig. 13).

Chlorobenzenesulfonamide (2), ring-opened carbamoyl guanidine (9), *O*-desmethylchlorsulfuron (6) and unidentified bound residues were the major metabolites of [*phenyl-U-<sup>14</sup>C]chlorsulfuron observed to form in detectable amounts. In this particular field study, the level of (2) increased rapidly from day 4 until the*





**Fig. 4.** Degradation of 158 g AI ha<sup>-1</sup> [phenyl-<sup>14</sup>C]chlorsulfuron and [triazine-2-<sup>14</sup>C]chlorsulfuron and formation of chlorobenzenesulfonamide and triazine amine (0–100% scale to left) and other key metabolites (0–30% scale to right) in the 0–10 cm layer of a field soil located in Moscow, ID.

123-day sampling and then appeared to plateau and decline slowly, comprising about 75% of initially applied radioactivity by the end of the experimental period. Detected initially at day 41, (9) appeared to reach a peak early in the study and then declined significantly by the end of the experimental period. Initial levels of (6) were detected early (first sampling) and remained low (<6% of applied radioactivity), declining to below detection limit by the 272-day sampling.

The results for [triazine-2-<sup>14</sup>C]chlorsulfuron were also similar to those for [phenyl-<sup>14</sup>C]chlorsulfuron in this study. The intact chlorsulfuron declined and fell below the detection limit by the 370-day sampling. The major metabolites formed in detectable amounts were triazine amine (3), (9), (6), hydroxy triazine amine (10), triazine urea (8) and unidentified bound residues. The dynamics of formation of (3) proceeded similarly to those of (2), increasing rapidly until the 123-day sampling and then declining slowly to comprise 60% of initially applied radioactivity by the end of the

experimental period. Levels of (9) showed a steady decline from the 60-day to 540-day period, falling to 5.1% of the initially applied radioactivity. The level of (10) peaked at the 272-day sampling and then quickly declined to below detection limit by the 370-day sampling. Detectable levels of (8) were found at the 14-day sampling and declined to below detection limit by the 370-day sampling, never reaching more than 5% of applied radioactivity. Although observed only at low levels in this study (and possibly at Madera, CA), its presence is indicative of a light-mediated mechanism<sup>30</sup> and suggests that either soil surface photolysis, or perhaps indirect photolysis, was operable. Formation of unidentified forms of radioactivity bound to soil appeared to plateau by the end of the experimental period and comprised approximately 22% of initially applied radioactivity for the [triazine-2-<sup>14</sup>C]- and 15% for the [phenyl-<sup>14</sup>C]chlorsulfuron. The higher levels of soil-applied radioactivity found in this form for the [triazine-2-<sup>14</sup>C]chlorsulfuron mirror behavior of

several of the laboratory studies, which suggested that microbes can degrade the triazine moiety more easily than the chlorobenzenesulfonamide moiety.<sup>30</sup>

### 3.2 Field mobility of chlorsulfuron and metabolites

#### 3.2.1 Mobility of fall versus spring applications

Dynamic mobility profiles of chlorsulfuron and its degradation products (as represented by total radioactivity) in *in-situ* soil columns are compared for the fall versus spring applications in Figs 4–7. It appeared that less precipitation was required following fall applications to move total radioactivity to a similar depth. Following fall application of chlorsulfuron to the neutral pH (6.9) site at Akron, CO (Fig. 5), significant detection at the 22–35 cm depth was made at the five-month sampling. Following the spring application, detection was made at this depth at the four-month sampling; however, only 117 mm of precipitation had fallen following the fall application versus 233 mm following the spring application. The profile found at the five-month sampling in the fall treatment was similar to that found at the 5–8-month sampling in the spring treatment, despite the fact

that it had received double the total precipitation. An interesting observation is that only 6 mm of precipitation resulted in a significant change in the distribution profile between months 4 and 5–8 in the spring treatment. With such major changes occurring after such low amounts of precipitation, it is likely that the intervals between samplings were too long to allow determination of subtle differences between treatments, making it debatable whether the ‘snapshot’ of distribution captured at a particular sampling was representative of a longer time period. A portion of the precipitation at all of the sites during the winter months is likely to have been received as snow and released at once during the spring thaw. These factors help make interpretation of mobility with precipitation more tenuous. Comparison of total radioactivity profiles in the soil over a longer period indicates that initial differences were moderated, as illustrated by the similar profiles 12 months after treatment.

An interesting phenomenon was observed at the alkaline Akron, CO site. It appeared that the total radioactivity recovered in the fall-applied cores increased nearly three-fold (from 15.3 to 44.0%) at the alkaline

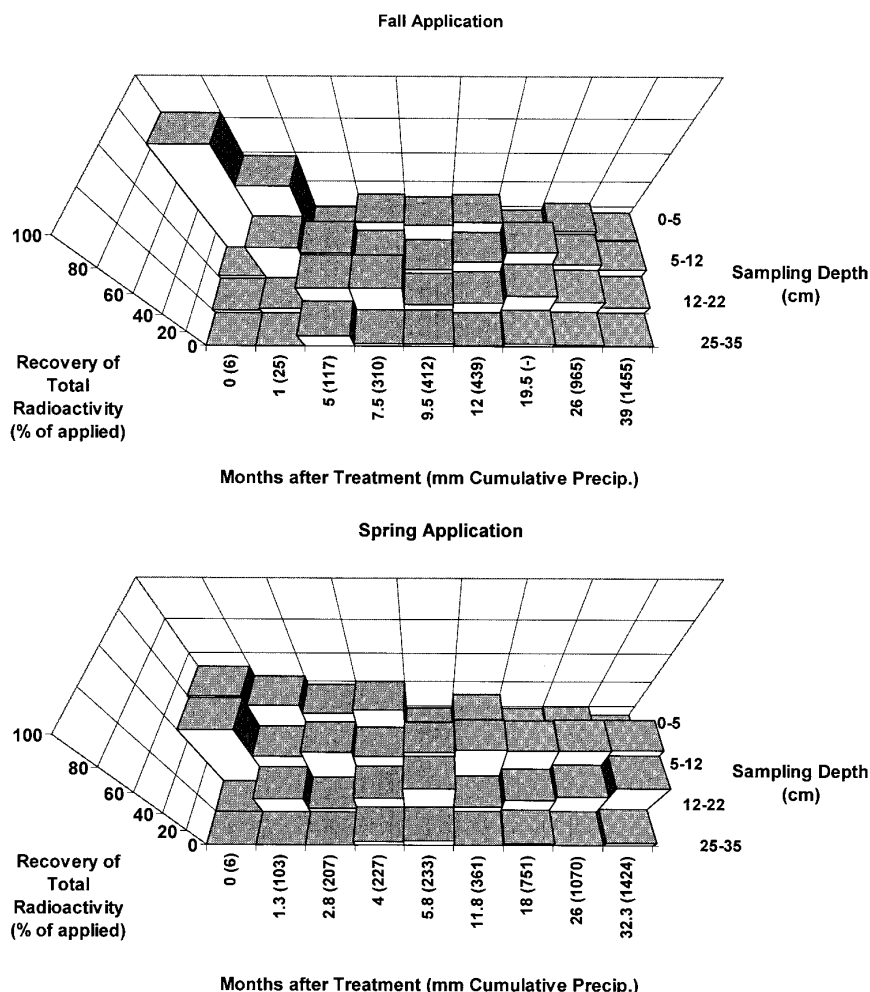
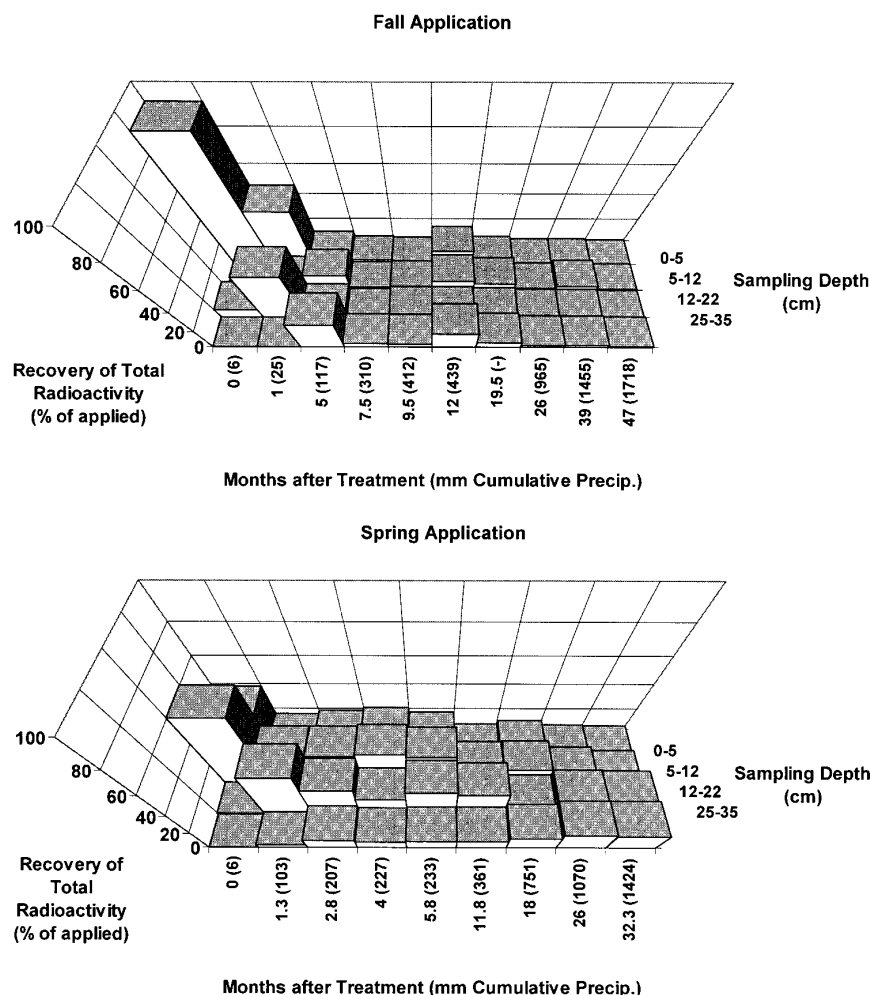


Fig. 5. Degradation of [phenyl- $U$ - $^{14}C$ ]chlorsulfuron and distribution of applied radioactivity with depth in Akron, Colorado (neutral site, pH 6.9).



**Fig. 6.** Degradation of [*phenyl-U-<sup>14</sup>C]chlorsulfuron and distribution of applied radioactivity with depth in Akron, Colorado (alkaline site, pH 8.2).*

pH site between the 9.5- and 12-month samplings, from Aug. to Nov. (Fig. 6). This may represent movement from lower depths through capillary rise, as demonstrated in soil columns<sup>37,38</sup> but not in the field; this study is acknowledged not to be definitive proof. This behavior was not duplicated in the spring-applied cores at that site, possibly because they retained relatively more total radioactivity. Because the columns were only 35 cm deep in these particular studies, with no deeper samples taken, it limited our ability to discern what occurred at greater depths.

A larger difference in distribution profiles between fall and spring applications was observed at the Kimberley, ID site on an alkaline soil with a pH of 8.0 (Fig. 7) and could be related to the amount of precipitation which fell. At six months after the spring application, no detectable radioactivity was seen at the 22–35 cm depth and only a minor amount was seen at the 12–22 cm depth, with most remaining in the top two layers after receiving 130 mm total precipitation. However, at four months after the fall application, which received slightly less precipitation (113 mm), most of the radioactivity was in the lower two layers. Similar to behavior at

Akron, CO, the difference in profiles between the fall and spring treatments diminished following intervals of 12 months or longer. At Fargo, ND on an alkaline soil (Fig. 8), depletion of the surface layer relative to lower layers was never observed in the spring treatment, whereas it was seen beginning at the 12-month sampling in the fall treatment and appeared to be maintained throughout the course of the study. The overall decreased rate of downward mobility here versus the other sites is probably related to the higher OM content (5.3%), and perhaps to the ability to see greater differences because of the slower dissipation. The results from these latter two sites in particular seem to support the concept of greater overall mobility from the soil surface layer previously observed in fall treatments.<sup>7,39</sup>

### 3.2.2 Mobility at Madera, CA

The mobility profile of the Madera, CA site shows that no radioactivity was observed leaching below 60 cm during the study (Fig. 9). This site (and the Moscow, ID site) was sampled to greater depths than the previously discussed mobility studies. Because no parent chlorsulfuron was detected beyond 120 days after treatment

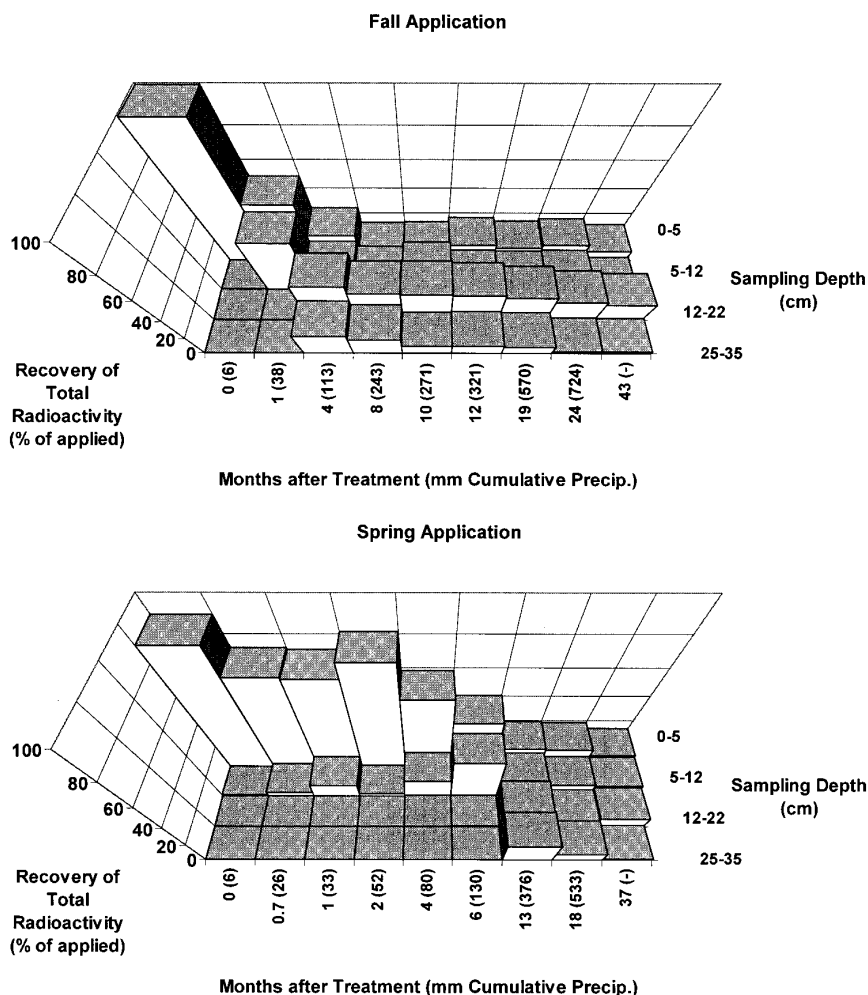


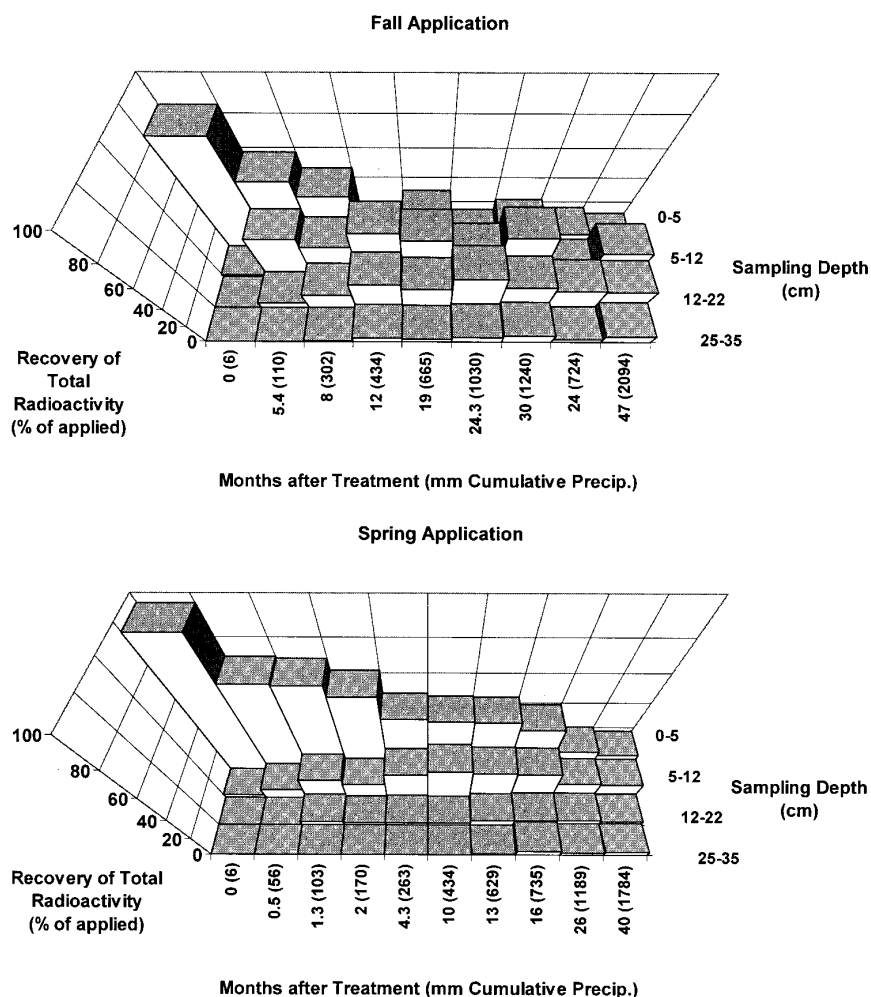
Fig. 7. Degradation of [*phenyl-U-<sup>14</sup>C]chlorsulfuron and distribution of applied radioactivity with depth in Kimberley, Idaho (pH 8.0).*

(Fig. 3), the interval between 120 and 540 days tracks the fate of its remaining metabolites. No intact chlorsulfuron was detected below 15 cm at any sampling, which can be attributed to its rapid degradation and potential to upward capillary movement, resulting in reaccumulation at the soil/air interface, a distinct possibility in this arid climate. The daily soil temperature maximum in the soil increased from below 20°C to 40°C during the first 120-day period that the chlorsulfuron parent molecule was detectable (Fig. 10). Despite bi-weekly irrigation which raised the total accumulation of water to 1011 mm, the cumulative water balance was still negative over the period (Fig. 11). This would have severely limited potential downward leaching and could have resulted in the capillary rise of chlorsulfuron. However, seen differently, a positive daily water balance occurred on 12 of the first 120 days at this location; each one can be considered as an opportunity for downward movement of chlorsulfuron and its metabolites. Presence of plant cover may have fostered deeper movement of chlorsulfuron and its metabolites through channeling through root pores, but may conversely have decreased the mass percolation through the soil through uptake

into the plant roots. The only period of significant groundwater recharge (approximately 200 mm) occurred between the mid-November and mid-February sampling points (sampling days 240, 300 and 331), corresponding to the period where the deepest leaching of total radioactivity occurred. The results indicated a low capacity for leaching deep into the soil profile or into groundwater by chlorsulfuron or its metabolites in this light-textured soil of low organic matter content under the climatic conditions observed during this study, despite the lack of plant interception (due to bare-ground application) and the irrigation which supplemented natural rainfall.

### 3.2.3 Mobility at Moscow, ID

The distribution of radioactivity was followed at Moscow, ID in the northwestern US (Fig. 12) on a heavier-textured soil than that at Madera, CA in a region less arid than the San Joaquin Valley of CA. No detectable radioactivity was found below the 50 cm depth at any sampling (versus 60 cm at Madera, CA). Intact chlorsulfuron was present until the 370-day sampling, much longer than at Madera, CA, and none was



**Fig. 8.** Degradation of [*phenyl-U-<sup>14</sup>C]chlorsulfuron and distribution of applied radioactivity with depth in Fargo, North Dakota (pH 7.6).*

detected below 10 cm, despite having received a total of 1028 mm water (Fig. 13). The slower dissipation can be explained by the lower soil temperatures seen at the Moscow, ID site. Soil pH levels were comparable between the two locations and would have affected hydrolysis and mobility similarly. Because of less loss through evaporation, the water volume available to percolate into the soil at the Moscow, ID site (Fig. 14) was higher than at the Madera, CA site, with more than double the positive net daily water balances (160 of 571 versus 69 of 539, respectively). Yet the distribution profiles remained similar. A relatively long period of potential groundwater recharge (of approximately 275 mm) between the early October and early June samplings (days 123, 272 and 370) did not appear to alter significantly the soil distribution of the total radioactivity. This can be explained by the fact that the ground was frozen during much of this period (Fig. 13) which prevented any potential movement until the spring thaw. More radioactivity was observed at the 15–30 cm depth (days 180–540) at Madera, CA than at the 10–20 cm depth at Moscow, ID. This suggests that the overall leaching of total radioactivity was less at Moscow, ID

than at Madera, CA, partly because of the winter freeze at the former site and because of the retarding effect of heavier texture and higher OM content on mobility at the latter site. The overall mass balance ranged from 74.4 to 175.6% during the study at Moscow, ID. The reason for this variability is not likely to have been application error, since the surfaces of the columns were treated individually. Perhaps differences in bulk density between the columns could have contributed to calculation of different concentrations of total radioactivity. No other explanation could be found.

### 3.2.4 Mobility in alkaline soils

Comparison of chlorsulfuron mobility between the fall applications to the neutral pH (6.9) and alkaline pH (8.2) sites at Akron, CO (Figs 4 and 5), shows that the total radioactivity retained in the soil columns appears to be higher in the neutral pH soil, as would be predicted. A greater proportion of the total radioactivity five months after the fall application was recovered from columns at the neutral site (93%) than at the alkaline site (58%); furthermore, nearly double was found at the 22–35 cm depth in the alkaline-pH site (27.4%) than in

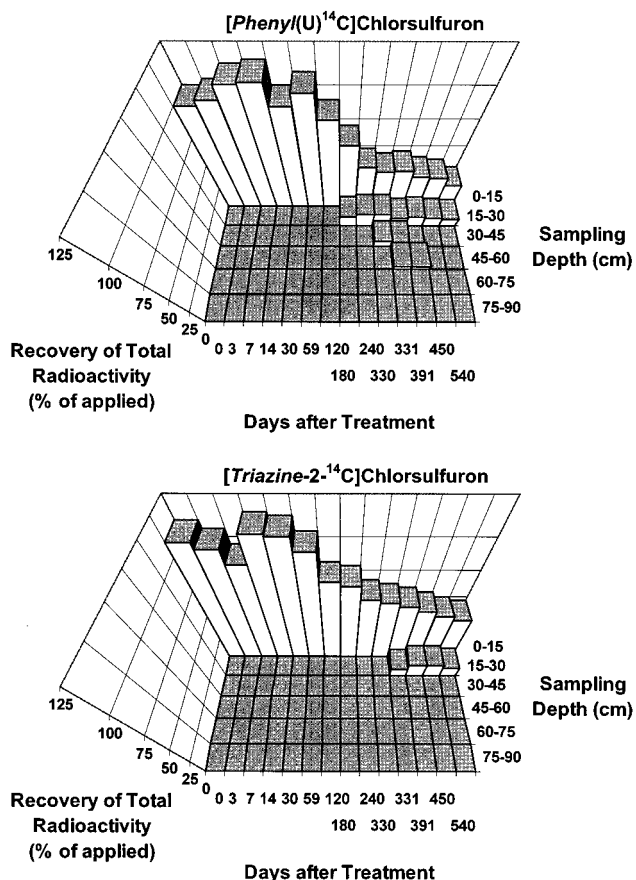


Fig. 9. Degradation of  $[^{14}\text{C}]$ chlorsulfuron and distribution of applied radioactivity with depth in Madera, CA.

the neutral-pH site (14.9%) at that sampling. Accordingly, a lower proportion was found at the 0–5 cm depth in the alkaline versus neutral soils (8.7% versus 18.7%, respectively).

Because significant levels of total radioactivity were found at the greatest sampling depth during the course of the studies at the sites on alkaline soils, a determination of the maximum depth of chlorsulfuron leaching was not possible. It is important to note that the maximum depth of the soil columns in these studies (35 cm) is only slightly deeper than the plow layer. Thus the dynamics of movement by chlorsulfuron in highly alkaline soils remain unclear and require more definitive work using chemical assay methods. Much of the investigation of the maximum depth of chlorsulfuron leaching in alkaline soils has been conducted using bioassays to measure chlorsulfuron. Vicari *et al.*,<sup>9</sup> using a *Nasturtium officinale* R. Br. bioassay, presented evidence of chlorsulfuron movement down to the 30–50 cm depth in soils at four sites (pH 7.8–8.2), but did not analyze any deeper. At one of the sites on a highly alkaline silty clay soil (pH 8.0), the bioactivity remained confined to the top 10–30 cm. Using a *Lupinus angustifolius* L. bioassay, Stork<sup>29</sup> speculated that 46% of applied chlorsulfuron leached below 50 cm in an alkaline soil (pH 8.5 surface increasing to pH 9.5 at 40–50 cm). However, in the bioassay used to quantitate chlorsulfuron, the overall growth of lupin in the controls appeared to decline significantly with depth, as did the magnitude of the plant response to chlorsulfuron, suggesting that the bioassay species was being adversely affected by a soil factor in addition to the herbicide concentration (possibly Na or B). The  $\text{ED}_{50}$  values appeared to shift with depth, implying that the chlorsulfuron was substantially more phytotoxic in the deeper soil layers. Furthermore, the bioassay curve used to interpret concentrations at the 40–50 cm depth contained only

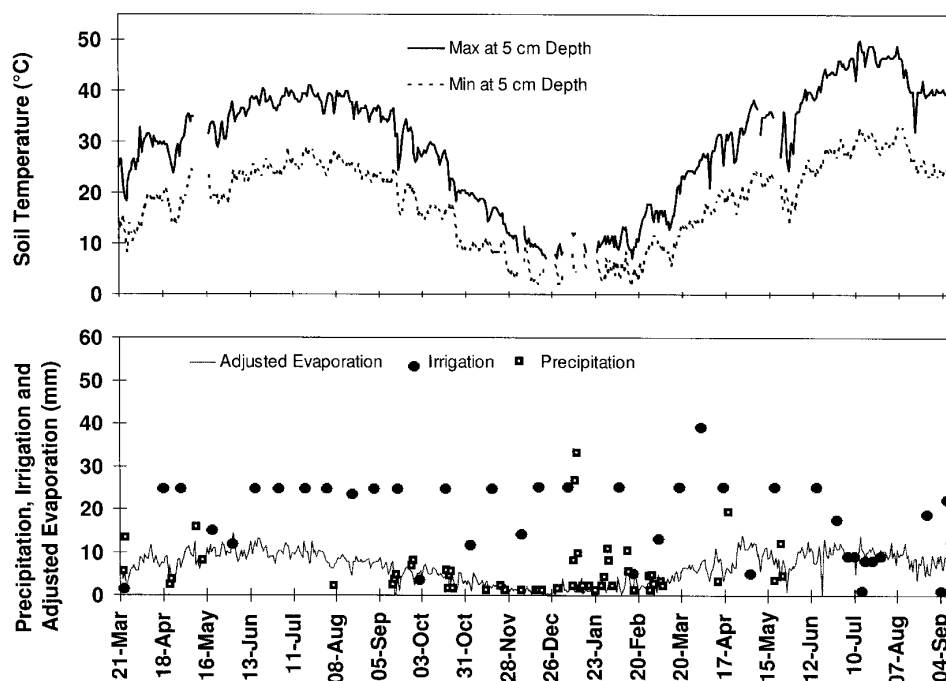


Fig. 10. Weather conditions at the Madera, CA site over the course of the 540-day experiment.

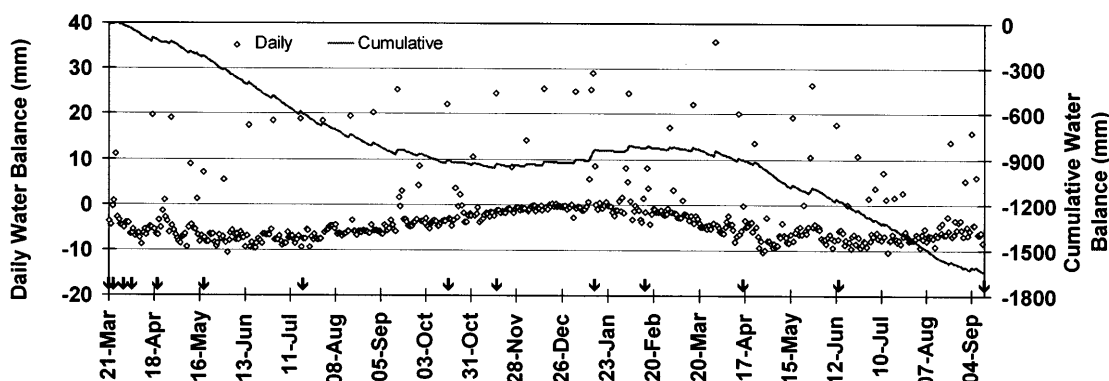


Fig. 11. Calculated water balance at the Madera, CA site over the course of the 540-day experiment. Arrows "↓" show sampling dates.

one point in the linear decline portion, with some extrapolations made outside this section. Thus, the results of this study cannot be considered conclusive. It is tempting to speculate that the perceived increase in  $ED_{50}$  values with depth could be due to formation of complexes of negatively charged chlorsulfuron with cations (i.e.  $Ca^{2+}$ ) under extremely alkaline conditions, resulting in greater uptake into the plant as an

uncharged complex, thus potentially increasing its phytotoxicity. However, a bioassay using chlorsulfuron solutions containing 0.005 M  $Ca^{2+}$  did not find any increase in the relative phytotoxicity to *Hordeum vulgare* L.<sup>40</sup>

Using an immunoassay to determine chlorsulfuron concentration, Nordh-Christerson and Bergström<sup>24</sup> found that most of the applied chlorsulfuron remained in the top 10 cm over a growing season at three sites in Sweden, one of them a moderately alkaline (pH 7.4) clay loam. Using liquid chromatography to assay chlorsulfuron, a study in Russia on a soil in which pH was modified by liming demonstrated that most of the treated chlorsulfuron remained in the top 5 cm in all treatments, but that the maximum depth of leaching increased from 10 to 35 cm as pH changed from 5.4 to 8.3.<sup>28</sup> In a field study conducted on two Swiss soils (pH 7.3–6.9 and 7.0–7.5 with depth) treated in the fall with triasulfuron, a sulfonylurea similar in structure to chlorsulfuron, leaching following 90 mm of irrigation was observed to a maximum depth of 90 cm in plots which remained wet before treatment versus to a maximum depth of 50 cm in plots kept dry prior to treatment.<sup>41</sup> The potential for greater leaching in alkaline soils appears to be tempered by the effects of alternate wetting and drying cycles on the movement and adsorption of chlorsulfuron. Although greater mobility of the chlorsulfuron molecule in alkaline soils is theoretically possible, other factors, such as the effect of evaporation on water balance in arid regions, must be taken into account.

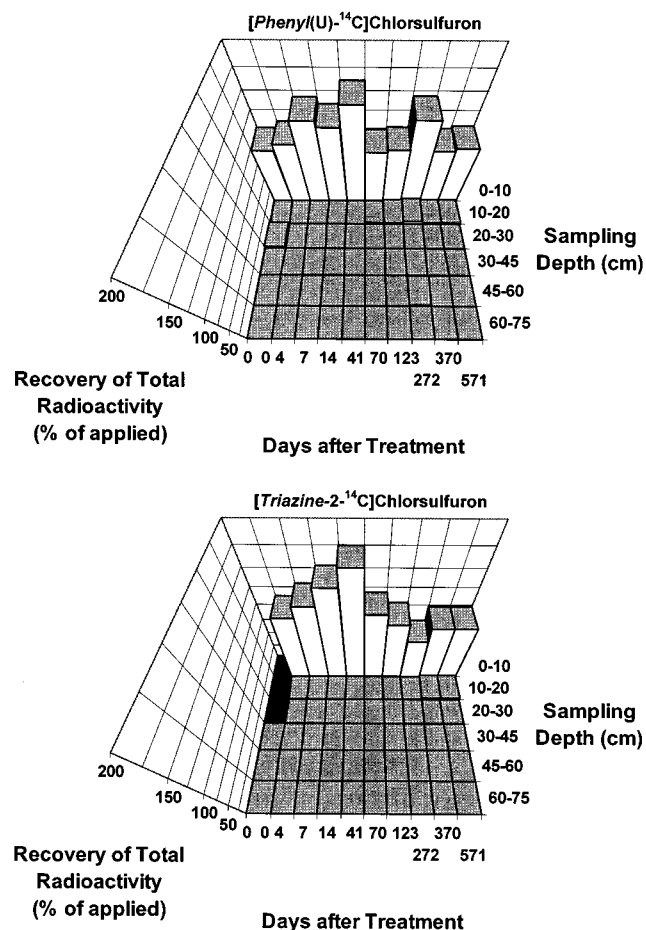


Fig. 12. Degradation of  $[^{14}C]$ chlorsulfuron and distribution of applied radioactivity with depth in Moscow, ID. The 0-day cylinder for the  $[triazine-2-^{14}C]$ chlorsulfuron was inadvertently not treated.

### 3.3 PRZM3 model predictions

Figure 15 illustrates a comparison of the actual soil concentrations of chlorsulfuron at the Moscow, ID site and those predicted by PRZM3, a model which 'simulates water and chemical movement in unsaturated soil systems within and below the plant root zone.'<sup>31</sup> The base modeling case, which utilized the actual weather data and measured bulk density ( $1.1 \text{ g cm}^{-3}$ ) from the

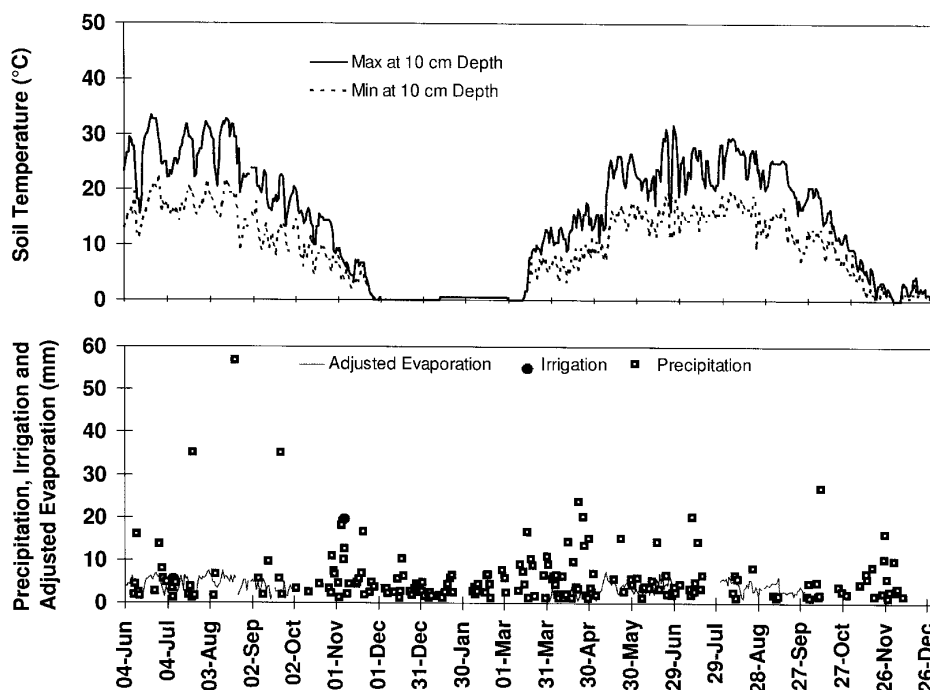


Fig. 13. Weather conditions at the Moscow, ID site over the course of the 571-day experiment.

site and actual chlorsulfuron dissipation rates calculated from the experiment (18 and 109 days), and the highest  $K_{oc}$  value (54) from laboratory absorption experiments,<sup>30</sup> overestimated downward movement of chlorsulfuron. It predicted that by the 123-day sampling, low levels of chlorsulfuron had moved down to the 10–20 cm depth, and by the 272-day sampling down to the 20–30 cm depth, and that the 0–10 cm zone had been depleted. The depletion in the surface layer of English soils was predicted using PRZM2 for not only chlorsulfuron,<sup>15,16</sup> but also for metribuzin, an asymmetrical triazine considered highly mobile in soil.<sup>42</sup> A prediction using the LEACHM model suggested that chlorsulfuron could move down to 70 cm in a loam soil in north-west Tasmania and down to 30 cm in a clay soil located at a much drier site in New South Wales.<sup>43</sup> Using a mechanistic dual-porosity model, Bergström<sup>44</sup> pre-

dicted that 0.3% of the applied chlorsulfuron could potentially leach to a depth of 70 cm after 11 months and determined that dissipation rate was important in allowing for a simulation that gave predictions close to actual lysimeter results.

The actual field data showed that chlorsulfuron was not detected below the 0–10 cm depth at any sampling. When the modeling parameters were modified by using a value of  $1.3 \text{ g cm}^{-3}$  for the bulk density, more in line for a soil of this texture,<sup>31</sup> the prediction improved slightly (not shown), displaying movement down only to the 10–20 cm depth but still showing depletion of the 0–10 cm layer. When the  $K_{oc}$  value of 54 was arbitrarily doubled to 108, it resulted in a much better prediction of the overall distribution profile. Movement down to the 10–20 cm zone was still predicted, but no depletion occurred in the 0–10 cm zone. The model predicted an

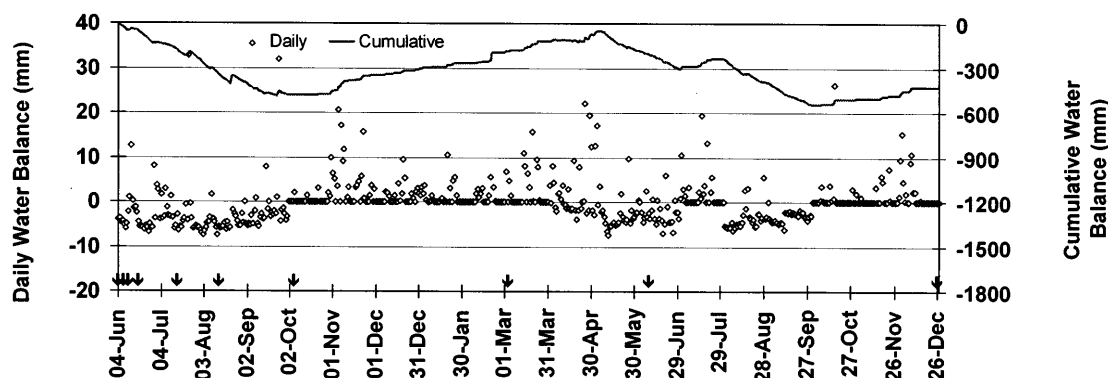


Fig. 14. Calculated water balance at the Moscow, ID site over the course of the 571-day experiment. Arrows "↓" show sampling dates.



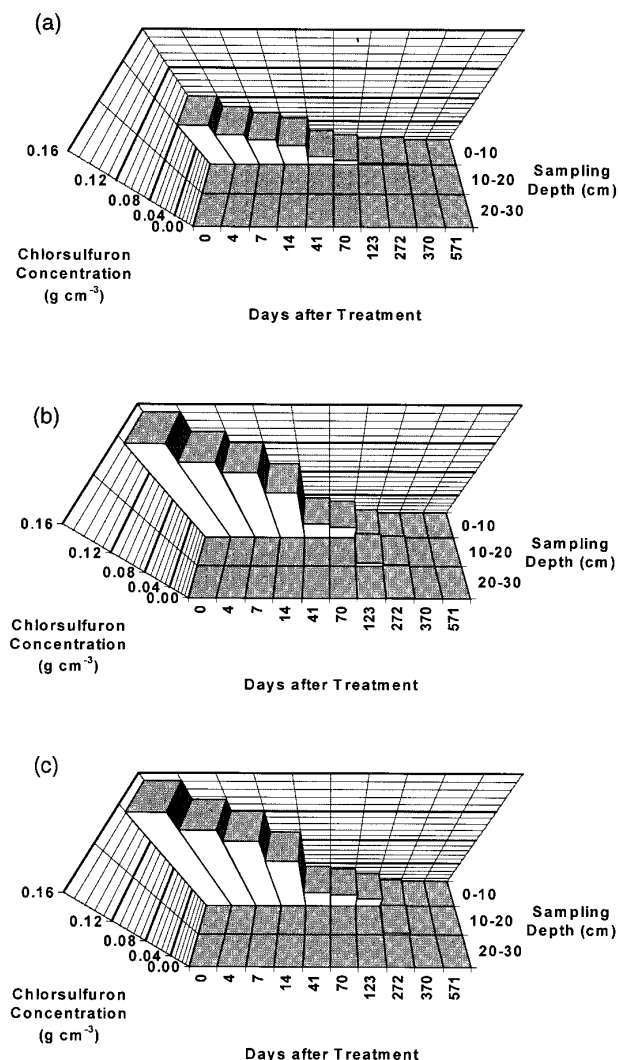


Fig. 15. Actual chlorsulfuron soil concentration distribution profile over time (a) at the Moscow, Idaho Site, (b) Base Case and (c) Best Case predictions by PRZM3.

average chlorsulfuron concentration twice that actually found in the field except at the 272-day sampling, where it was closer to the concentration found. It accurately predicted that chlorsulfuron would be non-detectable at the 370-day sampling. Walker<sup>13</sup> found that, when assuming an increase in soil adsorption with time, predictions of vertical distribution of propyzamide improved versus assuming a constant partitioning between adsorbed and solution phases. Equations developed to predict the long-term equilibrium partition coefficient for simazine (approximately 10-fold greater than in batch equilibrium experiments) markedly improved the prediction of its distribution profile in a field lysimeter experiment.<sup>45</sup> A striking increase in amount of adsorption with time has been observed for the structurally related sulfonyleurea metsulfuron-methyl, where increase of sorption in a laboratory experiment over a 30-day period was 10-fold greater than that measured in a batch experiment with the standard 24-h equilibration period.<sup>46</sup> This type of behavior

is not unlikely for chlorsulfuron. Additionally, in field applications, the more rapid degradation of a chemical in the soilwater through microbial degradation than in protected compartments within the soil matrix will result in a relative distribution or sorption skewed towards the soil phase, driving up the apparent value of the partition coefficient.<sup>33</sup> Therefore the increase in the  $K_{oc}$  value can be justified by experience with other sulfonyleureas; however, the amount of increase in chlorsulfuron sorption with time remains an area for further research.

The PRZM2 model was designed to predict leaching of a chemical through the soil profile and was not designed to predict chemical remaining in the soil surface.<sup>32</sup> Although PRZM3 can adjust the volume of percolating water lost through evapotranspiration, it does not include a component of upward capillary rise, which may be an important mode of transport in soil for chlorsulfuron under certain conditions.<sup>37,38</sup> With a notable number of the net daily water balances at the Moscow, ID site being negative during the summer (Fig. 14), it may be postulated that capillary rise could have occurred at this site and transported some of the chlorsulfuron from lower depths to the surface. The detection of the triazine urea (8) in the uppermost soil layer, suggesting the presence of a light-mediated degradation process, lends credence to this theory. Using a model which included a component of upward mobility, downward movement of chlorsulfuron in a laboratory study simulating fall applications in columns of alkaline clay loam soil (pH 8.1) was initially predicted to be less than that measured, and with time was predicted to be more than that measured.<sup>10</sup> The overprediction of downward movement, despite the inclusion of the upward movement component in the model, was attributed to the limitation of the physical length of the soil column (50 cm) interfering with the capacity for capillary rise to occur. Thus it is not clear how this component could be calibrated in the development of potentially useful constants for models. A potential shortcoming of using the PRZM3 model for predicting soil concentrations near the surface is that it uses batch equilibrium  $K_d$  values, which do not adequately describe desorption of chemicals by the soil in the field,<sup>47</sup> and may contribute to overprediction of mobility. With the aforementioned changes in input parameters, the model ultimately adequately predicted chlorsulfuron movement in the soil. No modeling of the mobility of the metabolites was attempted.

#### 4 CONCLUSIONS

The evidence from these studies indicates that fall-applied chlorsulfuron treatments did not persist any

longer into the following year than spring-applied treatments. A greater degree of mobility of chlorsulfuron and its metabolites into the soil profile may ensue in the months immediately following a fall application, but the difference between fall and spring treatments appears to moderate after several months. The greater mobility in soils with higher pH was clearly seen in the difference in behavior between the neutral and alkaline soils at Akron, CO. Since fall applications of chlorsulfuron to cereal crops are typically made in areas with acidic soils and most areas with alkaline soils typically receive spring applications, the practical significance of the increased potential for leaching of fall chlorsulfuron applications is lessened.

It was particularly clear from the study at Moscow, ID, that the chlorobenzenesulfonamide (2) and the triazine amine (3), products of cleavage of the sulfonylurea bridge, were the major soil metabolites in field soil. At Madera, CA ring-opened carbamoyl guanidine (9) was the only other metabolite which could be quantitated. Minor metabolites detected at the Moscow, ID site were ring-opened carbamoyl guanidine (9), *O*-desmethylchlorsulfuron (6), hydroxy triazine amine (10) and triazine urea (8). Although capillary rise has never been demonstrated *in situ* in a field soil, it is postulated to be able to facilitate chlorsulfuron accumulation at the soil-air interface, which potentially could result in soil-surface photolysis, perhaps an undervalued dissipation mechanism for chlorsulfuron used in arid, sunny climates. This is an area which would benefit from more research. Unidentified bound residues were always detected in higher amounts in the [*triazine-2-<sup>14</sup>C*]-labeled chlorsulfuron treatments, which suggests that, as in the laboratory studies,<sup>30</sup> the triazine moiety is more susceptible to microbial attack than the chlorobenzene-sulfonamide moiety.

Although chlorsulfuron could be classified as being moderately to highly mobile, based upon laboratory adsorption/desorption, soil TLC and soil column leaching studies,<sup>30</sup> and has demonstrated mobility to lower depths in field studies under certain conditions,<sup>15,16,28</sup> the results of field studies reported herein demonstrated that the mobilities of chlorsulfuron and its major soil metabolites were less than might be predicted. Climatic factors such as precipitation and temperature must be factored into mobility appraisals. An accounting of the water balance may be particularly effective in helping to determine the potential for leaching at a particular site. The laboratory study which appeared to come closest to qualitatively approximating the chlorsulfuron distribution profile in the field was the aged column leaching experiment.<sup>30</sup> Using alternate wetting and drying cycles in this type of experiment, such as experienced by field soils, would probably have improved the approximation even more.<sup>48</sup> Adsorption values derived from laboratory experiments resulted in overprediction of chlorsulfuron leaching in a PRZM3 model simulation,

which demonstrates that care must be exercised when using purely laboratory-derived inputs in models predicting field behavior.

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